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On the origin of the internal pressure in metals

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In order to describe the change ΔV of the atomic volume V of a solid with a change Δp of the external pressure the present writer (1) introduced the formula

$$(\alpha+\Delta p)(\beta+\Delta V)=\alpha\beta \tag{1}$$

analogous to the Boyle-Mariotte law. α was called pressure parameter and β volume parameter. In principle these parameters can be determined by compressibility measurements. Thus α is given by

$$\frac{2}{\alpha}=V_0\frac{d\varkappa}{dV} \tag{2}$$

where $\varkappa$ is the compressibility coefficient

$$\varkappa=-\frac{1}{V_0}\frac{dV}{dp} \tag{3}$$

and V_0 is the atomic volume at $p=0$. The parameter β is then obtained as

$$\beta=V_0\alpha\varkappa \tag{4}$$

The parameters α and β are also, at least approximately, simply related to other physical properties of the solids. Thus 2α was found to equal the proportionality factor between the energy of lattice vibrations and the increase of volume due to thermal expansion. β, the compressible part of the atomic volume, gives a simple understanding of the approximate constancy of the Grüneisen γ which was found to equal $V/2\beta$. α and β together also seem to determine the energy of activation for self-diffusion. In the following we shall look for the origin of the pressure α.

The simplest assumption which can be made about α is that it is the pressure from the cohesive forces counterbalancing the expansion due to the pressure caused by the movements of atoms and free electrons. According to the virial theorem we should thus have

$$\alpha=\frac{2}{3}\frac{E}{V} \quad \text{or} \quad E=\frac{3}{2}V\alpha \tag{5}$$

where E is the kinetic energy of the particles. In metallic conductors E is a sum of contributions from the positive ions and the free electrons and each of these parts is a sum of contributions from zero-point energy and thermal energy. Of these four contributions the zero-point energy of the electrons is the dominating one. For instance, it constitutes in copper at room temperature 98,7 % of the total energy. For the present the uncertainty of α and E is far above one per cent and for a first check of equation (5) we can confine ourselves to the approximation

$$E \approx E_{\mathrm{elz}} \tag{6}$$

where E_{elz} means the zero-point energy of the free electrons.

E_{elz} can be calculated from the electron specific heat, which is obtainable by calorimetric measurements in the helium range of temperature, and which in recent years has been determined for a great many metals. According to the Fermi-Sommerfeld theory this specific heat is per mole

$$C = \gamma T \tag{7}$$

with

$$\gamma = \nu N \frac{\pi^2 k^2 m}{h^2} \left(\frac{4 \pi g}{3 n} \right)^{\frac{2}{3}} \tag{8}$$

Here ν is the number of free electrons per atom, N the number of atoms pro mole, k the Boltzmann constant, m the electron mass, h the Planck constant, g the Landé factor and n the density of electrons. For E_{elz} the theory gives

$$E_{\mathrm{elz}} = \nu N \frac{3 h^2}{10 m} \left(\frac{3 n}{4 \pi g} \right)^{\frac{2}{3}} \tag{9}$$

Combining the equations (8) and (9) we get

$$\frac{E_{\mathrm{elz}}}{\nu^2} = \frac{3 \pi^2}{10} N^2 k^2 \frac{1}{\gamma} \tag{10}$$

We thus obtain E_{elz}/ν^2 from γ without the use of m and n, which is very fortunate because these factors are theoretically uncertain. n is the number of free electrons divided by the volume available for their movements which is an unknown fraction of the total volume. The same uncertainty is often ascribed to the electron mass m which is replaced by an effective mass m^*, different from m.

In order to check equation (5) we have on the one hand calculated E_{elz} by means of the equations (5) and (6) from experimental values of α and V, and on the other hand E_{elz}/ν^2 by means of equation (10) from experimental values of γ. The control of our fundamental assumption will be whether the collation of E_{elz} and E_{elz}/ν^2 gives reasonable values for the valency numbers ν.

The pressure parameters α_0 at zero pressure are according to equation (2) determined from the initial slope of curves describing the compressibility coefficient $\varkappa$ as a function of the relative volume V/V_0, the $\varkappa$-values being obtained from published tables of V/V_0 for varying pressures p. For the highly compressible metals we are mainly dependent on the measurements of Bridgman in the range of pressures below 100 kb. An earlier survey [1] gives examples of the way in which the α-values are determined and references to the many publications of Bridgman. For a number of less compressible metals new results obtained by shock-wave technics in the pressure range of about 150–500 kb published by Rice, McQueen and

	α_0 kb	V $\frac{\text{cm}^3}{\text{mole}}$	E_{elz} $\frac{\text{kJ}}{\text{mole}}$	γ $\frac{\text{mJ}}{\text{mole deg}^2}$	E_{elz}/ν^2 $\frac{\text{kJ}}{\text{mole}}$	ν
3 Li	57	13.0	111	1.82	113	1.0
4 Be	1050	4.9	780	0.226	910	0.9
11 Na	25	23.7	89	1.80	114	0.9
12 Mg	80	14.0	168	1.35	152	1.0
13 Al	230	10.0	345	1.35	152	1.5
19 K	14	45.5	96	1.97	104	1.0
20 Ca	75	25.9	292	3.08	66	2.1
22 Ti	690	10.7	1110	3.34	61	4.3
24 Cr	570	7.3	620	1.40	147	2.1
25 Mn	95	7.5	107	13.8	15	2.7
26 Fe	660	7.1	700	5.0	41	4.1
27 Co	1080	6.7	1080	5.0	41	5.1
28 Ni	1280	6.7	1280	7.0	29	6.6
29 Cu	295	7.1	314	0.69	297	1.0
30 Zn	210	9.2	290	0.64	320	1.0
40 Zr	(800)	14.0	1680	2.95	70	(4.9)
41 Nb	(700)	11.0	1150	8.5	24	(6.9)
42 Mo	(1400)	9.4	1970	2.14	96	(4.5)
45 Rh	(600)	8.4	760	4.2	49	(3.9)
46 Pd	(750)	9.3	1040	9.9	21	(7.0)
47 Ag	206	10.3	317	0.66	310	1.0
48 Cd	156	13.0	304	0.71	290	1.0
49 In	130	15.8	308	1.81	113	1.7
50 Sn	270	16.3	660	1.75	117	2.4
73 Ta	(1000)	11.2	1680	3.4	60	(5.3)
78 Pt	(1000)	9.1	1370	6.8	30	(6.7)
79 Au	200	10.2	310	0.74	277	1.1
81 Tl	100	17.3	260	3.1	66	2.0
82 Pb	90	18.3	247	3.0	68	1.9
90 Th	160	11.7	281	4.7	44	2.5

Walsh [2] give, in some cases in connection with results from Bridgman's measurements, a basis for an estimation of the α-values. The α-values thus obtained are collected in the table, together with the atomic volume V at room temperature and calculated values of E_{elz}. These are obtained by means of the equations (5) and (6), which give

$$E_{\text{elz}} = 0.15\,\alpha\,V \tag{11}$$

if α is in kilobar, V in cm³/mole and E_{elz} in kJ/mole. The α-values have all a rather high percentual uncertainty. In cases where this uncertainty is thought to be more than ± 20 % the values are in brackets.

In recent years the electron specific heats have been measured at low temperatures for many metals. A critical compilation of the results was given by Keesom and Pearlman in 1956 [3], from which we have taken most of the γ-values given in the table. The others are from later publications. Thus the values for Li and K are from Roberts [4], Al from Phillips [5], Ca and Cu from Griffel, Vest and Smith [6], Zn from Seidel and Keesom [7], Sn from Corak and Satterthwaite [8], Ta from Clusius and Losa [9], Pd from Rayne [10], Cr and Ni from Rayne and Kemp [11], and Th from Smith and Wolcott [12]. The variation of the results obtained by different authors for the same metal shows that the percentual uncertainty is appreciable also in the case of γ. From the γ-values we have calculated the values of E_{elz}/ν^2, shown in the table, by means of equation (10) which may be written

$$\frac{E_{\mathrm{elz}}}{\nu^2}=\frac{205}{\gamma} \tag{12}$$

if γ is in mJ/mole deg^2 and E_{elz} in kJ/mole.

The table contains in all 30 metals, for which data are available for both α and γ. There are a few other metals for which only one of these quantities has been determined. With the present great activities in the fields of low temperatures and high pressures there are good prospects that a table of this kind will be obtained in a few years which will be much more complete and accurate. The ν-values in the last column of the present table have an uncertainty of at least 10 %.

Nevertheless, it is evident already from this preliminary survey, that the valency numbers ν obtained give good support to the theory. Within the limits of errors we find as should be expected $\nu=1$ for Li, Na, K, Cu, Ag, and Au. An interesting result is that the elements Be, Mg, Zn, and Cd in the second group of the periodic system seem to produce only one free electron pro atom in the metallic state, while Ca, as might be expected, produces two free electrons. The interpretation of the high ν-values obtained for certain transition elements must be a subject for future consideration.

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